

ANISOTROPY AND MICROSTRUCTURE OF HIGH-COERCIVITY RARE EARTH PERMANENT MAGNETS

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by

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carried out on a JEOL 200 CS analytical transmission electron microscope equipped with a high take-off energy dispersive (EDS) X-ray analyzer. *key words →*

Nd-Fe-B based magnets have good hard magnet properties at room temperature. Minor substitutions (such as Dy, Al, Ga, Nb) increase the intrinsic coercivity H_c at room temperature and therefore also increase the operation temperature of the magnet up to 120°C. A Co-substitution, which causes a remarkable increase of the Curie temperature T_c , causes an improvement of the hard magnet parameters in rapidly quenched material only. The complex, multiphase microstructure and the coercivity of $Nd_2Fe_{14}B$ based sintered magnets is influenced by doping the magnet. In doped sintered magnets the dopant is dissolved in the hard magnetic ϕ -phase. If the solubility of the dopant is low, precipitates are formed within the ϕ -phase. Dopants also form new intergranular phases and influence the wetting of the liquid phase and the smoothness of the surface of the ϕ -grains during sintering. The purpose of this study was to investigate the effect on anisotropy, microstructure and coercivity by the substitution of Nd by other rare earth elements, such as Pr and Dy and Fe by Co, and by doping the magnets by Al, Al_2O_3 , Nb, Mo, Zr and Ga. Up to now no new compounds were found which have magnetic properties which can solve the problems at elevated temperatures really. Therefore further research on this field is still necessary in order to achieve a high quality permanent magnet with an operating temperature up to 150°C.

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1. INTRODUCTION

In $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based permanent magnets the coercivity is in practice only 20 - 40 % of the theoretical limit. The aim of this study was to investigate Nd-Fe-B based compounds with respect to their anisotropy behaviour. It is well known now that $\text{R}_2\text{Fe}_{14}\text{B}$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Dy}, \text{Tb}$) is a hard magnetic compound which was important for the development of a new family of Co-free permanent magnets.

Our investigations concentrated on the one hand on the investigation of the anisotropy behaviour of this group of materials and on the other hand on the microstructure of sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based magnets. The temperature dependence of the magnetic anisotropy provides valuable information about the origin of the anisotropy and at the same time it gives a first hint about the technical relevance of a certain compound.

Several micromagnetic theories to explain the coercivity have been developed. All of these theories are based on a two-dimensional "model-microstructure" and determine the equilibrium state of lowest free energy. A number of empirical microstructural parameters can be deduced from these theories: a description of the magnetic decoupling and misalignment of hardmagnetic grains, the effect of inhomogeneity of the magnetocrystalline anisotropy on nucleation and pinning and the local demagnetization factor which can be partly correlated with the grain size of the material, and other parameters.

The application of R-Fe-B based magnets is limited by the low Curie temperature of the hard magnetic phase $\text{RE}_2\text{Fe}_{14}\text{B}$, which results in a high temperature dependence of the coercive field. The high irreversible thermal losses are reduced and the reversible temperature coefficient of the remanence B_r is increased by partial substitution of Co for Fe and Dy for Nd and by adding small amounts of additional elements. The high magnetocrystalline anisotropy at room temperature of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ (\odot)-phase primarily determines the intrinsic coercivity. Substituents such as Dy which increase the anisotropy field, effectively increase the coercive field. A high magnetocrystalline anisotropy is a necessary but not a sufficient condition for achieving high coercive fields. The microstructure of the magnetic material influences strongly and in some cases even determines the coercivity. Another possibility to enhance the coercivity is the addition of small amounts (<1 wt.%) of dopants, such as Al, Nb, Zr, Mo, Ga or other refractory elements. The influence of the dopants on the coercive field is not fully understood but it is agreed that the increase of coercivity (up to 30%) is due to a microstructural effect in cases where the anisotropy field changes only slightly.

2. ANISOTROPY STUDIES OF HIGH COERCIVITY RARE EARTH - IRON PERMANENT MAGNETS

2.1 Experimental

The anisotropy field H_A was determined by using the SPD (Singular Point Detection) technique. For this purpose polycrystalline samples are sufficient. It should be mentioned that this technique yields the physically relevant anisotropy field without need for complex mathematical evaluation. All measurements were performed in a pulsed field system which was designed and built in our laboratory. Our equipment allows measurements between 4.2K and 1000K. The maximum available field is 280 kOe; the pulse duration of a sinus half wave is 5ms. The field is produced in a copper coil (inner diameter 18 mm) reinforced by a glass fiber construction. Most of the samples were obtained from other groups (e.g. Prof. Buschow) or companies (e.g. Hitachi). If permanent magnets were available the temperature dependence of the hysteresis loop (and consequently the coercivity H_{1c} and the remanence M_r) were also measured in pulsed fields. This provides values of H_A and H_{1c} for the same sample and for a technically relevant composition. This technique therefore allows a correlation between H_{1c} and H_A in order to verify coercivity models as will be shown here.

2.2 Results

2.2.1 $R_2Fe_{14}B$ compounds

The temperature dependence of the anisotropy fields of various $R_2Fe_{14}B$ ($R = Y, La, Ce, Pr, Nd, Gd, Ho, Lu$ and Th) was measured. The magnetocrystalline anisotropy in materials for which the R component has an orbital moment consists of two different contributions with opposite temperature dependence. All compounds investigated in this project are uniaxial at room temperature. At temperatures well below the Curie temperature the 4f sublattice anisotropy decreases with temperature while the 3d lattice anisotropy increases with temperature. Attempts to measure the anisotropy field for the compounds with $R = Dy$ and Tb were not successful. Even at room temperature it is too high. The compounds with $R = Nd$ and Pr gave H_A values between 70 and 80 kOe around room temperature which is reasonably high for making permanent magnets.

$Ce_2Fe_{14}B$ has a remarkable lower ordering temperature due to the tetravalence of Ce and in addition the anisotropy field is below 25 kOe. All this results in the fact that a magnet made mainly of the Ce -compound is not very useful.

The temperature dependence of the initial susceptibility of all $R_2Fe_{14}B$ compounds including the elements $R = Sm, Dy, Er$ and Tm was also measured between 4.2K and 300K. A spin reorientation was found for $Nd_2Fe_{14}B$ and $Ho_2Fe_{14}B$ but not for $Pr_2Fe_{14}B$. For $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$ a FOMP (First Order Magnetization Process) anomaly below 200K was observed. These results are in good agreement with single crystal data.

In a simple model the initial susceptibility scales with the reciprocal of the magnetic anisotropy. This is indeed valid for the $R_2Fe_{14}B$ compounds. If the material is not uniaxial this will cause an increase in domain wall mobility giving rise to remarkably larger values of the initial susceptibility.

2.2.2 Investigations on mixed crystal systems

2.2.2.1 $Nd_2Fe_{14-x}Co_xB$

The temperature dependence of the anisotropy field of $Nd_2Fe_{14-x}Co_xB$ was measured between 77K and the Curie temperature. The anisotropy field at room temperature was found to decrease with increasing Co content. Measurements of the temperature dependence of the initial susceptibility showed that at a certain temperature T_1 below room temperature the easy axis of magnetization does no longer lie exactly parallel to the c-axis but lies in a cone. The origin of this change is attributed to the Nd sublattice anisotropy. For the Co-rich samples ($x \geq 5$) it was found that at a certain temperature T_2 above room temperatures a second spin reorientation takes place, caused by the competing effects of the Nd sublattice anisotropy and the 3d sublattice anisotropy. The full magnetic phase diagram was obtained.

Attempts to analyse the magnitude of the initial susceptibility χ_i by assuming that χ_i is proportional to the reciprocal of the anisotropy failed because other important metallurgically determined effects dominate χ_i . A comparison of the concentration dependence of H_A as obtained by the SPD technique with the one deduced from an extrapolation method demonstrates the importance of higher order anisotropy constants and the necessity of the SPD technique. A normalised plot of the temperature dependence of the anisotropy field shows a systematically increasing slope of (dH_A/dT) with increasing amount of Co (4). This is of great importance for applications of Co substituted materials.

2.2.2.2 $Pr_2Fe_{14-x}Co_xB$

The concentration dependence of the Curie temperature, the magnetization, the anisotropy field and the lattice parameters of $Pr_2Fe_{14-x}Co_xB$ for $0 \leq x \leq 1$ were measured. Both the

c and a lattice parameters decrease with increasing amount of Co. The Curie temperature increases strongly with x. This is valid for all Co substituted systems. The saturation magnetization at 4.2K decreases with x after remaining approximately independent of the concentration up to $x = 0.2$. The room temperature anisotropy field decreases with x, but increases strongly with x after passing through a minimum at about $x = 0.7$. This increase of H_A which is strongly pronounced at low temperatures specially for the Pr-system, is not yet fully understood. The strong decrease of the c/a ratio on the Co rich side might be responsible for this unusual behaviour. In compounds with higher Fe contents the high field magnetization curves measured with the magnetic field perpendicular to the alignment direction show a field induced FOMP transition, indicating the importance of higher order anisotropy constants in these materials (6). The concentration dependence of the anisotropy constants K_1 , K_2 and K_3 at 4.2K was deduced from high field magnetization measurements.

2.2.2.3 $\text{La}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$

The concentration dependence of the Curie temperature, magnetization, anisotropy field and lattice parameters in $\text{La}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ for $0 \leq x \leq 14$ was measured. The anisotropy field was measured as a function of temperature in the range between 4.2K and the Curie temperature. The temperature dependence of H_A shows for Co concentrations $x > 2$ the usual decrease with increasing temperature. The concentration dependence of H_A shows a sharp decrease for small Co concentrations. For $x > 11$ an easy plane was detected in $\text{La}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$. No temperature induced spin reorientation was found in this system, indicating the band like behaviour of the 3d magnetism in this system. The complex anisotropy behaviour is very probably a consequence of the different contributions to the anisotropy of the six different lattice sites in the 3d sublattice (13).

2.2.2.4 $\text{Nd}_2\text{Fe}_{14-x}\text{Z}_x\text{B}$ ($\text{Z} = \text{Al}, \text{Si}, \text{Ga}, \text{Co}, \text{Ni}$)

Almost every element which replaces Fe in $\text{Nd}_2\text{Fe}_{14}\text{B}$ lowers the magnetocrystalline anisotropy. The effect on the ordering temperature T_c is different: in particular Al and Ni reduce T_c , whereas Si, Ga and Co increase T_c . Mössbauer experiments show that the Fe atoms are substituted in a non random manner. This is supported by the change in magnetic properties found for various substituents.

In the systems $\text{R}_2\text{Fe}_{14-x}\text{Ga}_x\text{B}$ ($\text{R} = \text{Nd}, \text{Pr}, \text{Gd}, \text{Y}$) the magnetic ordering temperature T_c increases along with x ($x < 1$) up to $T_c \approx 30\text{K}$. A similar behaviour is found for Si substitution which is remarkable, since Ga and Si are nonmagnetic

substituents. In the case of Si this finding can be explained by a preferential substitution of Fe by Si. On the other hand the addition of Al was found to lower the magnetic ordering temperature. The substitution of Fe commonly causes a reduction of T_c by up to 30K. For the samples with $Z = \text{Fe, Co, Ni}$ the values of H_A are the same within the experimental error. Al causes a drop in H_A , whereas Si and Ga lead to an increase. The rise in H_A which for Al and Ga substituted magnets is more than 50% compared to pure Nd-Fe-B cannot be explained by such small changes of the anisotropy. It should be mentioned that the change of H_A and T_c indicate that a part of the substituent enters the lattice of the hard magnetic phase. However, this is not an important factor for the increase of the coercivity. It seems that metallurgical effects are responsible to a large extent. This means that either the addition of nonmagnetic elements causes precipitates within the grains or it changes the intergranular boundary phase drastically (e.g. by leading to a smoothening of the grain boundary). The exact mechanism of this enhancement of the coercivity is not completely understood and therefore subject to further studies.

In order to clarify the role of the different substituents, systematic ^{57}Fe Mössbauer studies were carried out. The binary precipitations are larger for $Z=\text{Ga}$ (6%) and Ni (8%), for the remainder; they occur in amounts of less than 4%. The Nd-rich phase remains below 3%. Considering the analysis of the Mössbauer spectra with respect to a deviation from a random Fe substitution, attention is focused to those subspectra arising from the lattice sites with the largest occupation numbers, i.e. k_1 , k_2 , j_1 and j_2 . According to the weak intensity the hyperfine parameters for the c and a sites are known only within a relatively large error. For the k and j sites a strong preference in either direction can be found; in any case the k_1 -site is preferentially occupied by Fe, the k_2 -site by the substituent. As a whole the k sites are preferred by the substituents; in the case of $Z = \text{Ni}$, Si a preference of Fe for the j-sites is found. A distinct difference between the j-sites is obtained for $Z = \text{Al}$ and Ga (Fe prefers the j_1 -site, Z the j_2 -site). The discussion shows that a preferential occupation alone cannot cause the different effects of the substitution of Fe on T_c and H_A . Comparing the results might hints to an explanation of the enhancement of the anisotropy field: a preference of the substituent for the k-sites and a preference of Fe for the j-sites favours larger H_A values (15). Besides the preferential substitution the change of lattice constants (c/a ratio) because of the substitution might also contribute to this behaviour of the anisotropy. To look further into this studies of variations of lattice constants and thermal expansion are in preparation.

3. MICROSTRUCTURE STUDIES OF HIGH COERCIVITY RARE EARTH - IRON PERMANENT MAGNETS

The microstructural investigations were undertaken to show the influence of dopants, in particular of Al-dotation on the microstructure and coercivity of $\text{Nd}_2\text{Fe}_{14}\text{B}$ based sintered magnets.

3.1 Experimental

The magnet samples investigated were commercial grade magnets in peak aged condition of the general nominal composition $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$, but prepared under different conditions and partly containing small amounts of Dysprosium and of dopants (< 1wt.%) such as Al, Al_2O_3 , Nb, Zr, Mg and Dy_2O_3 , respectively. The intrinsic coercivities of these magnets ranged from 300 kA/m till 2500 kA/m. The magnets were produced by various producers (Hitachi Met., Shin-Etsu Chem.Comp. and Sumitomo Spec.Met., Japan, CISRI Beijing, China, Crucible Materials and Unocal, USA) under different processing and post-sintering heat treatment conditions. Doped, "two-phase" $\text{Nd}_{20}\text{Fe}_{81}\text{B}_{1.5}:(\text{Al};\text{Al}_2\text{O}_3)$ sintered magnets were prepared by the Max-Planck-Institut für Metallforschung, Stuttgart, FRG and a $\text{Pr}_{15}\text{Fe}_{82.5}\text{Co}_{1.5}\text{B}_{1.5}\text{Al}$ sintermagnet was prepared by the Carnegie Mellon University, Pittsburgh, USA. A mechanically alloyed Nd-Fe-B magnet sample was supplied by Siemens, Erlangen, FRG.

The magnets were investigated by optical metallography and analytical TEM in order to identify the multiphase microstructure. The magnets were examined in a JEOL 200 CX scanning transmission electron microscope (STEM) fitted with a LaB_6 filament, a high take off-angle energy dispersive X-ray analyzer (EDS). A beryllium double tilt specimen stage was used to reduce background intensities. All X-ray spectra were analyzed using the quantitative software program for thin samples.

3.2 Results

In Nd-Fe-B sintered magnets a nonmagnetic layer phase between the hardmagnetic ϕ -grains is desirable in order to increase the expansion field of reversed domains and to decrease the coupling field between neighbouring grains originated by magnetic stray fields. Individual, large softmagnetic phases in the form of precipitates or inclusions such as α -Fe or Fe-rich phases, extremely deteriorate the intrinsic coercive field and have to be avoided.

In principle, small softmagnetic precipitates within the Φ -grains could act as domain wall pinning centres, if the density and size of precipitates were optimized. In fact, no sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based magnets with effective domain wall pinning were reported so far.

We have extensively studied the microstructure of sintered Nd-Fe-B magnets and our investigations revealed at least five different types of phases in addition to the hardmagnetic Φ -phase. Several Nd-rich phases with different Nd/Fe ratios are found preferentially as intergranular phases at grain boundary junctions and extending to grain boundaries. Our TEM studies show that two types of grain boundaries occur in Nd-Fe-B sintermagnets: grain boundaries (GB1) without any intergranular phases and grain boundaries (GB2) composed of nonmagnetic Nd-rich phases. Two types of Nd-rich intergranular phases with minor Fe-content are found. The phase (n1) with a high dislocation density exhibits a fcc crystal structure with $a=0.52$ nm, whereas phase (n2) exhibits a hcp crystal structure with $a=0.39$ nm and $c=0.61$ nm which was determined by electron diffraction. Within the interior of the (n2) phase only individual dislocations are visible. Analytical TEM investigations reveal a remarkable difference of the X-ray spectra. With decreasing Fe content (< 5 at.%) the Nd-rich phase changes from the fcc (n1) to the hcp (n2) crystal structure. Al_2O_3 -doped magnets contain an increased amount of the (n2) phase.

Our TEM investigations in some cases revealed Nd-rich intergranular phases with a higher iron content than the (n1)-phase and an unknown crystal structure and also a platelet shaped phase (p1) with an approximate composition of $\text{Nd}_5\text{Fe}_2\text{B}_3\text{O}_7$ embedded in the (n1)-phase. Polycrystalline, spherical Nd_2O_3 -inclusions with diameters up to 500 nm are always present within the hardmagnetic Φ -grains as well as embedded in the intergranular phase.

If dopants are added to the prealloy or before sintering (in the form of oxides) in order to increase the coercive field, the microstructure is affected in a threefold way:

- (1) the dopant is dissolved in the hardmagnetic Φ -phase (changing the magnetocrystalline anisotropy ?)
- (2) precipitation within Φ -grains: Nb, Zr, Mo (possibly domain wall pinning?)
- (3) formation of new intergranular phases: Al, Nb, Mo (influences wettability and therefore magnetic coupling of grains)

The dopant element is always found to take the Fe-sites in the hardmagnetic Φ -grains. Energy dispersive X-ray microanalysis shows an additional $\text{AlK}\alpha$ -peak in the X-ray spectrum of the Φ -phase. A low solubility of the dopant element at sintering temperature leads to the formation of precipitates

enriched by the dopant such as in the case of Nb, Mo and Zr. In Al-doped sintermagnets no such precipitation was found. We found a Nb-precipitation within the Φ -grains in Nb-doped (Nd,Dy)-Fe-B magnets. Two types of precipitates were identified: the Laves phase type NbFe_2 having a MgZn_2 structure ($a=4.82$ nm and $c=7.87$ nm) and the FeNbB -phase.

Zirconium additions result in three different, partly coherent Zr-rich or Zr-containing precipitates within the Φ -grains. A similar precipitation behaviour was reported in Mo-doped Nd-(Fe,Co)-B magnets.

Dopants also form new intergranular phases and influence the wetting of the liquid phase and the smoothness of the surface of the Φ -grains during sintering and therefore affect the coercivity. The coercivity of Nd-Fe-B sintered magnets is increased by adding small amounts of Al or Al_2O_3 . Our study of such doped materials revealed a high amount of an Al-containing phase (al). From X-ray microanalysis we determined the composition of this phase as $\text{Nd}(\text{Fe},\text{Al})_2$ which is in accordance with data of the ternary phase diagram Fe-Al-Nd. High resolution electron microscopy showed the lattice fringe contrast corresponding to the crystal lattice planes of such an (al)-phase embedded between Φ -grains and (n1)-phases. The crystal structure and the crystal lattice parameters of this Al-containing phase are unknown at present. From the lattice fringe image of this phase a crystal lattice periodicity of approximately 1.2-1.4 nm was determined. It should be mentioned that our investigations never revealed any Al-enrichment of the Nd-rich phases (n1), (n2) and (p1). This result is in contrast with previously reported data which showed a partial enrichment of Al in the Nd-rich intergranular phase. Similar results of new Ga-rich phases in the intergranular regions were found in Ga-doped Nd-Fe-B sintered magnets.

Other Fe-rich phases and α -Fe precipitates within the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -grains as well as in Nd-rich intergranular regions were found in several magnets with decreased coercivity. Such phases are probably byproducts of an oxidation process.

3.3 Discussion of microstructural investigations

Sintering of Nd-Fe-B magnets is primarily determined by the liquid phase type of sintering mechanism which involves the presence of a low melting, viscous Nd-rich eutectoid. During sintering the driving force for densification of Nd-Fe-B magnets is the capillary pressure and the surface tension. Both, surface diffusion along grain boundaries and volume diffusion, play also an important role during densification. Liquid phase sintering occurs most readily when the liquid thoroughly wets the solid particles at the sintering temper-

perature. The liquid in the narrow channels between the particles results in substantial capillary pressure. The particle size, sintering temperature and time, the uniformity of particle packing, the particle shape and the particle size distribution are extremely important parameters. Fine particle size powder can be sintered more rapidly and at lower temperature than coarser powder. If particle packing is not uniform in the pressed "green" compact, it will be difficult to avoid porosity during sintering. Smaller particles exhibit a higher driving force for densification (higher capillary pressure and higher surface energy) than coarser particles. The rate of liquid phase sintering is strongly affected by the sintering temperature. A small increase in temperature results in a substantial increase in the amount of liquid present, but on the other hand this causes excessive grain growth, which deteriorates the magnetic hardness.

Densification during the liquid phase sintering process depends on two important parameters, the contact (wetting) angle and the dihedral angle. Generally, better liquid phase sintering is associated with smaller values of both angles. The wetting angle is a characteristic parameter which describes the balance between the interfacial energies of liquid, solid and vapor phases. It was shown that the wetting angle is in the order of 8° or smaller and decreases with increasing Al-content of the magnet. In order to get a high amount of intergranular phases good wetting between intergranular and ϕ -phases is favourable. The dihedral angle is formed where a solid-solid grainboundary intersects the liquid and is important to the microstructure of polycrystalline grains and to the contact of ϕ -grains in the liquid phase. In a first approximation the dihedral angle is estimated from the two-dimensional section of the three phase junction to be in the order of 20° at one corner. A high dihedral angle between the ϕ -grains during the liquid phase sintering process retains the liquid phase from penetration into the grain boundaries. For a dihedral angle over 60° the liquid becomes isolated at the triple points between grains and forms a continuous network along the three grain junctions. From our investigations we conclude that the constitution of the intergranular region is inhomogeneous and consists of several phases with different composition. This is in good agreement with our analytical TEM investigations with two types of grain boundaries (GB1) and (GB2) in a two dimensional section. Depending on the cooling rate and post-sintering heat treatments various Nd-rich phases (n) occur in the magnet. The formation of new intergranular phases positively influence the coercivity because the contact angle and the dihedral angle are decreased leading to a higher volume fraction of intergranular phases which separate the hardmagnetic ϕ -grains. In $\text{Nd}_2\text{Fe}_{14}\text{B}$ sintered

magnets both Nd-rich phases, the one with fcc (n1) and the one with hcp (n2) crystal structure, have been identified so far. The metastable (n1) phase is probably stabilized by additional elements. Our EELS investigations show an oxygen pick-up of this phase which is in accordance with Auger electron spectroscopic results of in situ fractured surfaces and EDS X-ray microanalytic results taken with an ultrathin window detector. Our systematic investigations show that besides oxygen also a small amount of Fe must be considered as stabilizing factor. With decreasing Fe content (< 5 at.%) the Nd-rich phase changes from the fcc to the hcp crystal structure.

The increase of the coercive field of the doped magnets $\text{Nd}_2\text{Fe}_{14}\text{B}(\text{Al}; \text{Al}_2\text{O}_3)$ is attributed to the presence of $\text{Nd}(\text{Fe}, \text{Al})_2$ and hcp Nd-rich phases because no change of the morphology and microstructure of the fcc Nd-rich phase (n1) is observed (no Al content). For the explanation of the increased coercivity two effects are essential: First, there is a better wettability of these phases compared to the fcc Nd-rich phase, thus the volume fraction of grain boundaries containing an intergranular phase is increased, leading to an increased magnetic decoupling of Φ -grains. Second, the smoothness of the surface of the hardmagnetic Φ -grains during the liquid phase sintering process is influenced. A similar effect was found in Dy_2O_3 -doped sintered magnets.

In conclusion, our TEM analysis indicates that the increase of the coercive field of doped $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based sintered magnets, in particular of Al-doped magnets, has to be attributed to the change of the constitution and the wettability by the intergranular phases. Coercivity is increased by a higher contiguity of the intergranular region (decoupling of hardmagnetic grains) and by suppression of nucleation sites for reversed domains (surface hardening of hardmagnetic grains).

4. COERCIVITY STUDIES OF HIGH COERCIVITY RARE EARTH - IRON PERMANENT MAGNETS

Sintered permanent magnets based on Nd-Fe-B were studied with respect to their hysteresis loop but also to their anisotropy field. These magnets were made by:

- a) Sumitomo Comp. (Dr. M.Sagawa)
- b) Colt Industry (Dr. K.S.V.L.Narasimhan)
- c) Philips Research Lab. (Prof. K.H.J.Buschow)
- d) Hitachi Metals Ltd. (Dr. H.Harada, Dr. M.Tokunaga)

The main problem in the field of permanent magnets is the development of a generally applicable coercivity model. Up to now two important models exist:

- i) Nucleation. Walls whenever present move easily.
- ii) Pinning at distortions (which can be impurities in the grains or the grain boundaries or precipitates).

The mechanism responsible for the coercivity determines the temperature dependence. A comparison between the experimental and a theoretical temperature dependence can show the validity of a certain model. For Nd-Fe-B based sintered magnets a nucleation dominated coercivity mechanism was found, which can be described by the following simple formula:

$$H_{ic}(T) = c.[H_n(T)] - N.M_s$$

H_n is the nucleation field (if the second order anisotropy constant is negligible, H_n can be replaced by the anisotropy field H_A). $-N.M_s$ is the demagnetizing field due to the neighbouring grains.

The aim of this part of the work was to prove respectively to modify existing coercivity models for Nd-Fe-B based permanent magnets. For this purpose the temperature dependence of H_{ic} , M_r and H_A was measured in order to find a correlation between these parameters.

4.1 Magnets produced by Sumitomo

The temperature dependence of the coercivity H_{ic} and the anisotropy field H_A from Nd-Fe-B based sintered magnets was measured between 100K and the Curie temperature. A $Pr_{1.5}Fe_{7.7}B_8$ magnet and a series of the composition $Nd_{12.5}Dy_{1.5}(Fe_{7.75-x}Co_x)B_7$ ($x = 0, 10, 20$) were studied in order to achieve improvements of the temperature characteristic above room temperature. The Co substitution increases the Curie temperature but it changes H_A at room temperature only slightly. The coercivity, however, is reduced drastically, so that the temperature behaviour of the sample with $x = 20$ is comparable to that of a pure Nd-Fe-B magnet. The best results in this respect were achieved with a heavy rare earth substituted material ($x = 0$) and with the $Pr_{1.5}Fe_{7.7}B_8$ sample. It was tried for the first time to correlate $H_{ic}(T)$ and $H_A(T)$ using two different models based on the formula

$$H_{ic}(T) = c.[(H_A(T))^k] - N.M_s$$

where k lies between $1/2$ and $5/2$; the best value of k characterizes the coercivity model. A temperature dependent k , lying between $3/2$ and $5/2$, reflects a mechanism which varies with the temperature. However, the assumption of a temperature independent M_s might be too restrictive (9).

4.2 Magnets produced by Colt

A similar study was carried out on sintered magnets produced by Colt Ind. (USA). The analysis of the $H_{ic}(T)$ and $H_A(T)$ curves using the same models resulted in k values lying between $3/2$ and $5/2$. This exponent generally decreases with decreasing temperature indicating either a temperature induced change of the coercivity mechanism or the influence of K_2 at low temperatures (5).

4.3 Magnets produced by Philips

A sintered Nd-Fe-B and a Nd,Dy-Fe-B permanent magnet were studied measuring $H_{ic}(T)$ and $H_A(T)$. The analysis was performed graphically plotting $H_{ic}(T)$ versus $H_A(T)$. A linear dependence of the coercivity on the anisotropy field was found to be valid in a broad temperature range (3,7).

4.4 Magnets produced by Hitachi

This was the most effective study because for these samples the composition as well as the heat treatment were varied in a systematic manner. The samples were sintered to give aligned magnets with the following compositions:

$Nd(Fe_{0.92}B_{0.08})_{5.5}$	
$(Nd_{1-x}Dy_x)(Fe_{0.92}B_{0.08})_{5.5}$	$x=0.1, 0.2, 0.3$
$Nd(Fe_{0.92-x}Co_xB_{0.08})_{5.5}$	$x=0.046, 0.092, 0.184$
$(Nd_{0.8}Dy_{0.2})(Fe_{0.92-x}Co_xB_{0.08})_{5.5}$	$x=0.092, 0.184$

Each sample was provided in the as sintered state (1090°C; 2 hours), but also after two heat treatments:

- i) 1090°C; 2 hours and 900°C 2 hours then cooling at 1.3°C/min
- ii) 1090°C; 2 hours and 900°C 2 hours then cooling at 1.3°C/min down to 600°C then quenched in water.

Additionally a set of sintered magnets of the composition:

$Nd(Fe_{0.92}B_{0.08})_z$	$z=4.0, 4.5, 5.0, 5.5, 6.2$
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was studied. Increasing z causes an increase of the distance between the grains as was shown by electron microscopy. From all samples the temperature dependence of the hysteresis loop (from which $M_r(T)$ and $H_{ic}(T)$ can be deduced) and also $H_A(T)$ was measured between 100K and the Curie temperature. The anisotropy field was measured in order to get an estimation for the nucleation field H_n (8,10).

4.5 Al-substituted magnets

These sintered magnets were produced by the Institute of Physics in Beijing (China). Introducing Al in Nd-Fe-B permanent magnets generally increases the coercive field. The temperature dependence of H_{ic} and H_A was measured for the system $Nd_{1-x}(Fe_{1-x}Al_x)_7B_2$ ($x = 0, 0.02, 0.04, 0.06, 0.08$) between 100K and the Curie temperature. The change of the anisotropy was small but detectable; H_A decreases with increasing amount of Al indicating that a part of the Al enters into the 2:14:1-structure. The spin reorientation, as detected at low temperatures, decreases with increasing Al content. The ordering temperature decreases also with increasing Al concentration. All these facts prove that a part of the Al enters indeed into the 2:14:1-lattice. The enhancement of the coercivity due to the Al substitution can not be explained by taking only the anisotropy behaviour into account. The "Al-effect" is therefore a consequence of the change in microstructure in these materials (10, 11).

4.6 Analysis

In an attempt to explain the temperature dependence of the coercive field a model is used based on the assumption that $H_{ic}(T)$ obeys a general formula of the type:

$$H_{ic}(T) = c \cdot [(H_A(T))^k (1 + aT) - N \cdot M_s]$$

The idea is to obtain information about different coercivity mechanisms by fitting the exponent k . The coupling constant c has the approximate value of 0.25. In the Dy and Dy₂Co substituted samples k is close to 1.0. The only Co substituted sample gave a k value of 1.25. The temperature dependence of k was found to be negligible. The value of the demagnetizing factor lies between 0.7 and 0.9. The heat treatment influences the demagnetizing factor N but not k .

The demagnetizing field acting between the grains should be sensitive to a variation of the distance between them. In order to verify this we investigated the second set of sintered magnets with a continuous variation of z (see Chapt. 4.4). The temperature dependence of H_A was found to be nearly independent of z which is a consequence of the small homogeneity range of the $Nd_2Fe_{14}B$ - compound. The temperature dependence of the coercivity field was again analysed using the model given above. The formula contains four free variables: c, k, a (a is the temperature coefficient of k) and N . The exponent k describes the coercivity mechanism. Holding one of these parameters constant and fitting the others shows that they depend strongly on each other. The most reliable results using this procedure were obtained with the following set of parameters:

$$c = 0.209 - 0.26; k=1 - 1.2$$
$$N = 0.5 - 0.74; a \approx 1.10^{-4}$$

Up to now no physically relevant correlation between the fitted parameters and the variable z could be found. A $\text{Sm}_2\text{Co}_{17}$ based magnet was analysed using the same model in order to test it. It is well known that the coercivity in these type of magnets is caused by pinning at precipitates. The analysis is performed in the following manner:

- i) the measured values of the coercive field are plotted as a function of the coercivity calculated in the framework of the present model.
- ii) they are then fitted assuming a linear relation between them. Finally plotting the corresponding standard deviation σ as a function of the coercivity a remarkable behaviour is observed comparing the different magnets:
 - a) The fit works well for a pure Nd-Fe-B based magnet (especially at higher temperatures). The $\sigma(H)$ curve shows a statistical spread.
 - b) In the case of a precipitation hardened 2:17 magnet as well as in a Dy substituted Nd-Fe-B magnet the $\sigma(H)$ curve is monotonic. This indicates that in the latter case the fit becomes less reliable.

In the case of a pinning type magnet H_a has to be replaced by H_p . The pinning field H_p depends critically on the ratio of the exchange energies and the anisotropy energies of the host lattice and the distortion. In this case it is clear that H_p cannot be replaced by the anisotropy field of the host material as was done here. From this analysis we conclude that for a pinning type magnet a different model which includes the intrinsic parameters of the precipitates also, has to be developed. However, it is difficult to determine these parameters experimentally (16).

5. DISCUSSION OF POSSIBLE IMPROVEMENTS OF Nd-Fe-B MAGNETS

The quality of modern permanent magnet materials is characterised by:

- a) High energy products $(BH)_{max}$. This is the relevant quantity which determines the achievable miniaturisation of magnetic components.
- b) High Coercive field H_{ic} . It is important for the stability of the magnetized state, especially in dynamic

applications.

- c) High Curie temperature T_c . It limits the temperature range in which the magnet can be used.

Nearly all these requirements were met with the development of magnets based on rare-earth - 3d compounds. They all have compounds a uniaxial crystal structure (hexagonal, tetragonal). The 3d-elements (Co or Fe) ensure a high ordering temperature; the rare earth elements cause a high (uniaxial) anisotropy (of Single Ion type). A uniaxial anisotropy is necessary for the formation of a reasonable coercivity. And clearly the "right" microstructure is important for a high coercivity. This is the general concept of rare-earth-3d permanent magnets.

Table I summarises the magnet parameters (typical values at room temperature) of the three magnet families in use.

Material	T_c [K]	M_s [kG]	H_A [kOe]	H_{ic} [kOe]	$(BH)_{max}$ [MGOe]
SmCo ₅	1020	11.2	300	20	25
Sm ₂ Co ₁₇	1195	12.8	65	12	30
Nd ₂ Fe ₁₄ B	580	16	75	10	40

M_s ...saturation magnetization; H_A ...anisotropy field.

It is evident that the Sm-Co magnets have an excellent thermal stability due to their high ordering temperature. However, the high costs of the raw materials are prohibitive for industrial large scale applications of these magnets. With the invention of the new Nd-Fe-B magnets it was possible to produce a cheaper, Co-free, high quality permanent magnet. The room temperature data are excellent but the rather low Curie temperature causes a fast decrease of H_{ic} with increasing temperature. For many technical applications (e.g. motors) a working temperature of up to 150°C is required. It should be mentioned that for a high temperature application the optimal working point which changes with temperature has to be taken into account. The $H_{ic}(T)$ temperature dependence is only a rough approximation and the irreversible losses which can occur in such a magnet are of great importance should it be operated for longer times at elevated temperatures. Great efforts are therefore undertaken to find improvements for the high temperature properties of high quality permanent magnets.

Concepts of improvements

5.1 Substitutions increasing T_c

When Fe is partly substituted by other metallic elements the ordering temperature T_c may increase or decrease. Ni and Si and also Ga increase T_c slightly but not Al. Mn and Cr may introduce an antiferromagnetic component. The most effective element is Co. From the phase diagram it can be seen that the compound $Nd_2(Fe_{0.8}Co_{0.2})_{14}B$ has a reasonably high T_c of more than 700 K. However, in a sintered Co substituted magnet H_{ic} decreases due to the Co substitution. The reason for this is not a reduction of the anisotropy field which is nearly constant on the Fe-rich side. A comparison to the behaviour of rapidly quenched Nd-(Fe,Co)-B (for which H_{ic} stays constant with small amounts of Co substitutions) shows that Co will unfavourable change the microstructure (intergranular phase) in the sintered magnets thus reducing H_{ic} . In addition to that the temperature dependence of H_{ic} (dH_{ic}/dT) becomes worse with the Co substitution. As mentioned already small amounts of elements like Si or Ga cause a slight increase of T_c . It is believed that this is a consequence of a preferential substitutions of some of the Fe sites. However, Si-substituted sintered magnets show a strong decrease of H_{ic} . Ga substituted sintered magnets gave a large increase of H_{ic} . This behaviour cannot be explained by the magnetic anisotropy; it must be an effect of the microstructure.

5.2 Substitutions increasing H_{ic}

These substitutions can be subdivided in elements causing an intrinsic increase of the magnetic anisotropy and those which enhances H_{ic} due to a metallurgical effect. To the first group belong mainly Tb or Dy, the latter group contains elements like Al or Ga.

5.2.1 Substitutions increasing H_A

The substitution of Dy causes a remarkable increase of H_A which is followed by an enhanced H_{ic} . In pure Nd-Fe-B as well as in Co substituted magnets the full coercivity is obtained only after a heat treatment. The concept that the improvement of H_{ic} is due to the larger H_A values is supported by the fact that for Dy containing magnets the influence of the heat treatment on the coercivity becomes negligible.

Because of the antiparallel coupling between Dy and Fe the

remanence M_r decreases with increasing amount of Dy. Dysprosium substituted magnets have a high coercivity at room temperature (approximately 20 kOe) and can therefore be used up to 150°C but the price for this improvement is a reduced energy product ($(B.H)_{max}$ is prop. to $B_r^2/4$).

Some investigators tried to combine the advantage of the Co substitution (increase of T_c) with that of the Dy- substitution (increase of H_{ic}). The temperature dependence of H_A of a set of samples of the composition $Nd_{1-x}Dy_x(Fe_{77.5-x}Co_x)B_7$ shows that between 200 and 400K $H_A(T)$ is quite similar. Only at higher temperatures ($T > 400K$) the effect of the increasing amount of Co becomes visible. Unfortunately this is not the case for the temperature dependence of H_{ic} . The higher Co content does not influence $H_{ic}(T)$! This means that at elevated temperatures the coercivity reducing effect of Co is stronger than the coercivity enhancing role of Dy. The temperature dependence of the remanence can be described to be approximately proportional to a Brillouin function. This means that the increase of T_c due to the Co substitution results in a better temperature character of $M_r(T)$. Therefore in summary a Dy- and Co-substituted material (which is more expensive) shows a better temperature behaviour up to 150°C but the magnet parameters at room temperature are nearly the same as those of a pure Nd-Fe-B magnet (especially with respect to $(B.H)_{max}$). Improvements along this direction are therefore not very convincing.

5.2.2 Nonmagnetic substitutions

Nonmagnetic substitutions such as Al or Ga also cause a remarkable increase of H_{ic} . Values of 16 kOe are reached with Al and 20 kOe with Ga. As already mentioned in Chapt. 4.6 the coercivity H_{ic} can be described in the following way:

$$H_{ic}(T) = c \cdot [H_A(T)] - N \cdot M_s$$

The addition of nonmagnetic elements may increase the thickness of an intergranular, nonmagnetic phase between the grains thus decoupling the grains and consequently reducing the demagnetizing field which causes an increase of H_{ic} .

5.3 New compounds

There are two new compounds worth mentioning:

- a) $R_2Fe_{14}C$. (R...rare earth elements). These compounds are isostructural with those containing B). The anisotropy field is remarkably higher than that of the B

compounds. Unfortunately, T_c is slightly lower ($T_c \approx 30K$) than in the case of the B compounds. Therefore a magnet based on this compound will not solve the temperature problem.

- b) Magnets based on the $ThMn_{12}$ compounds. Here only the Sm-containing material is of interest (uniaxial anisotropy); however, the highest Curie temperature found in this group of materials is $200^\circ C$ which is again too low for a high quality permanent magnet (17).

6. SUMMARY AND OUTLOOK

Nd-Fe-B based magnets are good magnets at room temperature. Substitutions increasing H_c at room temperature (such as Dy, Al, Ga) make magnet possible which can be used at temperatures up to $120^\circ C$. A Co-substitution resulting in a remarkable increase in T_c will bring an improvement of the magnet parameters in rapidly quenched material only. The complex multiphase microstructure and the coercivity of $Nd_2Fe_{14}B$ based sintered magnets can be controlled by doping the magnets. In doped sintered magnets the dopant is dissolved in the hardmagnetic ϕ -phase. If the solubility of the dopant is low, precipitates are formed within the ϕ -phase. Dopants also form new intergranular phases and influence the wetting of the liquid phase and the smoothness of the surface of the ϕ -grains during sintering. The purpose of this study was to investigate the effects of substitution of Nd by other rare earth elements, such as Pr and Dy and Fe by Co and of doping the magnets with Al, Al_2O_3 , Dy_2O_3 , Nb, Mo, Zr and Ga on anisotropy, microstructure and coercivity. Up to now no new compounds were found which have magnetic properties really solving the application problems at elevated temperatures. Therefore further research in this field is still necessary in order to achieve a high quality permanent magnet at reasonably low prices which can be used at $150^\circ C$ also.

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